NANOSTRUCTURES AND METHODS FOR

MANUFACTURING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the priority

5   of U.S. Provisional Application No. 60/393,835 filed

July 08, 2002, the entirety of which is incorporated

herein by reference, and of U.S. Provisional Application

No. 60/459,982 filed April 04, 2003, the entirety of

which is incorporated herein by reference.

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BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates generally to structures,

essentially in one-dimensional form, and which are of

15   nanometer dimensions in their width or diameter, and

which are commonly known as nanowhiskers, nanorods,

nanowires, nanotubes, etc.; for the purposes of this

specification, such structures will be termed " one-

dimensional nanoelements". More specifically, but not

 20   exclusively, the invention relates to nanowhiskers, and

to methods of forming nanowhiskers.

Brief Description of the Prior Art

The basic process of whisker formation on substrates, by the so-called VLS (vapor-liquid-solid) mechanism is well known. A particle of a catalytic

5   material, usually gold, for example, on a substrate is heated in the presence of certain gases to form a melt. A pillar forms under the melt, and the melt rises up on top of the pillar. The result is a whisker of a desired material with the solidised particle melt positioned on

10   top - see "Growth of Whiskers by the Vapour-Liquid-Solid Mechanism" - Givargizov - Current Topics in Materials Science Vol. 1, pages 79-145 - North Holland Publishing Company 1978. The dimensions of such whiskers were in the micrometer range.

15   International Application WO 01/84238 discloses in Figures 15 and 16 a method of forming nanowhiskers wherein nanometer sized particles from an aerosol are deposited on a substrate and these particles are used as seeds to create filaments or nanowhiskers. For the

20   purposes of this specification the term nanowhiskers is intended to mean one dimensional nanoelements with a diameter of nanometer dimensions, the element having been formed by the VLS mechanism.

Typically, nanostructures are devices having at least two dimensions less than about 1 μm (i.e., nanometer dimensions). Ordinarily, layered structures or stock materials having one or more layers with a thickness less than 1 μm are not considered to be nanostructures, although nanostructures may be used in the preparation of such layers, as is disclosed below. Thus the term nanostructures includes free-standing or isolated structures having two dimensions less than about 1 μm which have functions and utilities that are different from larger structures and are typically manufactured by methods that are different from conventional procedures for preparing somewhat larger, i.e., microscale, structures. Thus, although the exact boundaries of the class of nanostructures are not defined by a particular numerical size limit, the term has come to signify such a class that is readily recognized by those skilled in the art. In many cases, an upper limit of the size of the dimensions that characterize nanostructures is about 500 nm.

Where the diameter of a nanoelement is below a certain amount, say 50nm, quantum confinement occurs where electrons can only move in the length direction of

the nanoelement; whereas for the diametral plane, the electrons occupy quantum mechanical eigenstates.

The electrical and optical properties of semiconductor nanowhiskers are fundamentally determined by their crystalline structure, shape, and size. In particular, a small variation of the width of the whisker may provoke a considerable change in the separation of the energy states due to the quantum confinement effect. Accordingly, it is of importance that the whisker width can be chosen freely, and, of equal importance, is that the width can be kept constant for extended whisker lengths. This, together with the possibility of positioning whiskers at selected positions on a substrate, will be necessary if an integration of whisker technology with current semiconductor component technology is to be possible. Several experimental studies on the growth of GaAs whiskers have been made, the most important reported by Hiruma *et al*. They grew III-V nano-whiskers on III-V substrates in a metal organic chemical vapor deposition -MOCVD- growth system - *K. Hiruma, M. Yazawa, K. Haraguchi, K. Ogawa, T. Katsuyama, M.Koguchi, and H. Kakibayashi, J. Appl. Phys. 74, 3162 1993; K. Hiruma, M. Yazawa, T. Katsuyama, K.*

Ogawa, K. Haraguchi, M.Koguchi, and H. Kakibayashi, J. Appl. Phys. 77,4471995 ; E. I. Givargizov, J. Cryst. Growth 31,20 1975; X. F. Duan, J. F. Wang, and C. M. Lieber, Appl. Phys. Lett. 76, 1116 2000; K. Hiruma, H.

5 *Murakoshi, M. Yazawa, K. Ogawa, S. Fukuhara, M. Shirai,and T. Katsuyama, IEICE Trans. Electron. E77C, 1420 1994; K. Hiruma, et al, "Self-organised growth on GaAs/InAs heterostructure nanocylinders by organometallic vapor phase epitaxy", J. Crystal growth 163, (1996), 226*

10 *— 231.* Their approach relied on annealing a thin Au film to form the seed particles. In this way, they achieved a homogeneous whisker width distribution, the mean size of which could be controlled by the thickness of the Au layer and the way this layer transforms to nanoparticles.

15 With this technique, it is difficult to control the size and surface coverage separately, and it is virtually impossible to achieve a low coverage. The correlation between film thickness and whisker thickness was not straightforward, since the whisker width also depended on

20 growth temperature, and there were even signs of a temperature-dependent equilibrium size of the Au particles. The authors also noticed a strong correlation between the size of the Au droplets de-posited from a

scanning tunneling microscope tip and the resulting

whisker width. For the free-flying Si whiskers grown by

Lieber *et al.*,- *Y. Cui, L. J. Lauhon, M. S. Gudiksen, J.*

F. Wang, and C. M. Lieber, Appl.Phys. Lett. 78, 2214,

5   *2001* - a clear particle-whisker size correlation has been

shown.

       It is necessary, if whiskers are to be used as

electrical components, that there should be well-defined

electrical junctions situated along the length of a

10   whisker, and much work has been directed at achieving

this – see for example Hiruma et al, "Growth and

Characterisation of Nanometer-Scale GaAs, AlGaAs and

GaAs/InAs Wires" IEICE Trans. Electron., Vol. E77-C, No.9

September 1994, pp 1420-1424. However, much improvement

15   is necessary .

       Much work has also been carried out on carbon

nanotubes (CNTs). Despite progress, research has been

frustrated by a lack of control of the conductivity-type

of CNTs and an inability to form 1D heterostructures in a

20   controlled manner. Randomly formed interfaces as kinks

between metallic and semiconducting parts of CNTs have

been identified and studied (Yao et al, Nature, 1999,

402, 273) as have doping (pn) junctions in semiconducting

CNTs (Derycke et al, Nano Letters, 2001, *1*,453) and transitions between CNTs and semiconductor (Si and SiC) nanowhiskers (Hu et al, Nature, 1999, *399,* 48).

In a separate trend of development, attempts to
5   fabricate 1D devices have been made since the late 1980s by top-down methods, as pioneered by Randall, Reed and co-workers at Texas Instruments - M.A. Reed et al., Phys. Rev. Lett. 60, 535(1988). Their top-down approach, which still represents the state of the art for this family of
10   quantum devices, is based on epitaxial growth of multi-layers defining the two barriers and the central quantum well. Electron-beam lithography is then used to define the lateral confinement pattern, together with evaporation of the metallic layers to form the top
15   contact. A lift-off process is then used to remove the e-beam-sensitive resist from the surface, and reactive ion etching removes all the material surrounding the intended narrow columns. Finally, the devices are contacted via the substrate and from the top using a polyimide layer.
20   In the studies of devices fabricated by this bottom-up technique, 100-200 nm diameter columns have been observed, however, with rather disappointing electrical characteristics and peak-to-valley currents at best

around 1.1:1. An alternative approach to realizing low-dimensional resonant tunneling devices has been reported more recently, employed strain-induced formation of self-assembled quantum dots (I.E. Itskevich et al., Phys. Rev.

5 B 54, 16401(1996); M. Narihiro, G. Yusa, Y. Nakamura, T. Noda, H. Sakaki, Appl. Phys. Lett. 70, 105(1996); M. Borgstrom et al., Appl. Phys. Lett. 78, 3232(2001)).

SUMMARY OF THE INVENTION

10 The invention comprises a method of forming nanowhiskers, one-dimensional semiconductor nanocrystals, in which segments of the whisker have different compositions, for example indium arsenide whiskers containing segments of indium phosphide, wherein

15 conditions for growth allow the formation of abrupt interfaces and heterostructure barriers of thickness from a few monolayers to hundreds of nanometers, thus creating a one-dimensional landscape along which electrons can move. In a preferred method of chemical beam epitaxy

20 method (CBE), rapid alteration of the composition is controlled by the supply of precursor atoms into a eutectic melt of seed particle and substrate, supplied as molecular beams into the ultra high vacuum chamber. The

rapid switching between different compositions is
obtained via a sequence where growth is interrupted or at
least reduced to an insignificant amount, and
supersaturation conditions for growth are reestablished;
5   at least, change of composition and supersaturation is
changed faster than any appreciable growth. With abrupt
changes in material of the whisker, stresses and strains
arising from lattice mismatch are accommodated by radial
outward bulging of the whisker, or at least by lateral
10   displacement of the atoms in the lattice planes near the
junction.

Further, the invention includes a technique for the
synthesis of size-selected, epitaxial nano-whiskers,
grown on a crystalline substrate. As catalysts, size-
15   selected gold aerosol particles are used, which enables
the surface coverage to be varied completely
independently of the whisker diameter. The whiskers were
rod shaped, with a uniform diameter between 10 and 50 nm,
correlated to the size of the catalytic seed. By the use
20   of nano-manipulation of the aerosol particles, individual
nano-whiskers can be nucleated in a controlled manner at
specific positions on a substrate with accuracy on the nm
level. The method of the invention enhances width

control of the whisker by virtue of choice of nanoparticle. The nanoparticle may be an aerosol or a liquid alloy on the substrate may be made by starting from gold rectangles formed on the substrate which when

5   melted form accurate diameter balls. Other materials may be used instead of gold as the seed particle, e.g. Gallium.

Whilst it is desirable in many applications to have nanowhiskers which are essentially constant in diameter,

10   the shape of the whisker, and other attributes, may be varied by selectively changing the diffusion constant (diffusion coefficient) of the group III material , e.g. Ga, during whisker formation. This can be done by:

• Lowering the temperature of the process- this

15   produces whiskers tapered towards their free ends;

• Increasing the pressure of the group V material;

• Increasing the pressure of both group V and

20   group III materials.

More specifically, the invention provides a method of forming a nanowhisker comprising:

depositing a seed particle on a substrate, and exposing the seed particle to materials under controlled conditions of temperature and pressure such as to form a melt with the seed particle, so that the seed particle

5   melt rises on top of a column whereby to form a nanowhisker, the column of the nanowhisker having a diameter with a nanometer dimension;

wherein during the growth of the column, selectively changing the compositions of said materials whereby to

10 abruptly change the composition of the material of the column at regions along its length, whilst retaining epitaxial growth, whereby to form a column having along its length at least first and second semiconductor segment lengths, the first semiconductor segment being of

15 a material having a different band gap from that of the second semiconductor segment.

Functional 1D resonant tunneling diodes and other components and structures have been obtained via bottom-up assembly of designed segments of different

20 semiconductor materials in III/V nanowhiskers. Electronic and photonics components comprising nanowhiskers have also been formed as heterostructures, with a single crystal formation, wherein length segments

of the nanowhisker are of different materials, so as to create well defined junctions in the whisker between different band gap materials, whereby to create a component with a desired function.

5   Thus, the invention provides in general terms a heterostructure electronic or photonics component, comprising a nanowhisker having a column of a diameter with a nanometer dimension, the column having disposed along its length a plurality of length segments of
10   different material composition with predetermined diametral boundaries between adjacent segments extending over a predetermined length of the nanowhisker column, such as to give desired band gap changes at the boundaries, in order to enable the component to carry out
15   a desired function.

In a general aspect, the invention provides an electronic or photonic component, comprising a nanowhisker having a column with a diameter, which has a nanometer dimension,

20   the column comprising along its length at least first and second length segments of different materials with an abrupt epitaxial composition boundary disposed between the first and second segments, wherein lattice

mismatch at the boundary is accommodated by radial outward expansion of the nanowhisker at the boundary.

In another general aspect, the invention provides an electronic or photonic component, comprising a nanowhisker having a column with a diameter, which has a nanometer dimension,

the column comprising along its length at least first and second length segments of different materials with an abrupt epitaxial diametral material boundary disposed between the first and second segments, wherein the transition between the composition of the different materials of the first and second segments occurs over an axial distance of not more than eight diametral lattice planes. Preferably, the transition between the composition of the first and second segment occurs over an axial distance of not more than 6, lattice planes, preferably not more than 5 lattice planes, still more preferably not more than 4 lattice planes, still more preferably not more than 3 lattice planes, still more preferably not more than 2 lattice planes and most preferably not more than one lattice plane.

In a further aspect, the invention provides an electronic or photonic component, comprising a

nanowhisker having a column with a diameter which has a nanometer dimension, the column comprising along its length at least first and second length segments of different materials, the first segment having a

5   stoichiometric composition of the form $A_{1-x}B_x$, and the second segment having a stoichiometric composition of the form $A_{1-y}B_y$, where A and B are selected substances, and x and y are variables, wherein an epitaxial composition boundary disposed between the first and second segments,

10   comprises a predetermined gradual change from the variable x to the variable y over a predetermined number of diametral lattice planes. In a similar embodiment the compositions of the first and second segments of a nanowhisker of the invention can be represented by the

15   formulas $A_{1-x}B_xC$, and $A_{1-y}B_yC$, respectively, wherein A and B represent elements of one group, e.g., group III, of the periodic table, and C represents an element of another group, e.g., group V, of the periodic table. The variables x and y may assume a value between 0 and 1, and

20   represent different numbers within that range. Thus, such a nanowhisker is formed of a compound semiconductor that may vary in composition along its length, thereby incorporating a heterojunction. An example of such a

compound semiconductor is $Al_xGa_{1-x}As$. A nanowhisker of the invention may be constructed to have, e.g., two lengthwise segments, a first segment having a composition $Al_{1-x}Ga_xAs$, wherein the variable x has a given value between 0 and 1 and a second segment having a composition $Al_{1-y}Ga_yAs$, wherein the variable y has a second value different from the value of x. Between the two segments is an interface within which the composition varies continuously from the composition of the first segment to that of the second segment, i.e., the value of the variable x changes continuously, and usually monotonically, to the value of the variable y. This interface thus constitutes a heterojunction. The transition may be made to occur over a predetermined number of diametral lattice planes by adjusting the conditions under which the whiskers are grown, as will be explained in more detail below. Furthermore, the growth conditions can be periodically adjusted to produce a plurality of such heterojunctions along the length of the nanowhisker.

The diameter of the nanowhisker is controlled by the invention to be essentially constant along the length of the nanowhisker, or having a defined variation, such as a

controlled taper. This ensures precise electrical parameters for the nanowhisker, the controlled taper being equivalent to producing a voltage gradient along the length of the nanowhisker. The diameter may be small

5   enough such that the nanowhisker exhibits quantum confinement effects. Although the diameter is precisely controlled, there will be small variations in the diameter arising from the processing method, in particular a radial outward bulging of the nanowhisker at

10   a composition boundary in order to accommodate lattice mismatch in the epitaxial structure. In addition the diameter of one segment may be slightly different from that of another segment of a different material, because of the difference in lattice dimensions.

15   According to the invention the diameter of the nanowhiskers preferably will not be greater than about 500 nm, preferably not greater than about 100 nm, and more preferably not greater than about 50 nm. Furthermore, the diameter of the nanowhiskers of the

20   invention may preferably be in a range of not greater than about 20 nm, or not great than about 10 nm, or not greater than about 5 nm.

The precision of formation of the nanowhisker
enables production of devices relying on quantum
confinement effects, in particular a resonant tunneling
diode. Thus, an RTD has been developed wherein the
5 emitter, collector and the central quantum dot are made
from InAs and the barrier material from InP. Ideal
resonant tunneling behavior, with peak-to-valley ratios
of up to 50:1, was observed at low temperatures.

In a specific aspect, the invention provides a
10 resonant tunneling diode, comprising a nanowhisker having
a column of a diameter with a nanometer dimension, such
as to exhibit quantum confinement effects,

the column comprising along its length first and
second semiconductor length segment forming respectively
15 an emitter and a collector, and, disposed between the
first and second semiconductor segments, third and fourth
length segments of material having a different band gap
from that of the first and second semiconductor segments,
and a fifth central length segment of a semiconductor
20 material having a different band gap from that of the
third and fourth segments, disposed between the third and
fourth segments and forming a quantum well.

A problem which arises with an electrical or photonic component formed from a nanowhisker is that of making efficient electrical contacts to the nanowhisker.

One method is to remove the nanowhisker from its

5 substrate, by a mechanical scraping process, and to deposit the nanowhiskers on a further substrate, on their side lengthwise on the substrate. Metallised bond pads may then be formed over the ends of the nanowhisker, or alternatively the nanowhisker can be manipulated to be

10 positioned over preformed contact pads.

Alternatively, in a method which may be better suited to mass-production, the nanowhiskers may be left on the substrate, with their base ends having been formed on an electrical contact. Once formed, the nanowhiskers

15 may be encapsulated in a resin or glassy substance, and then contact pads may be formed over the surface of the encapsulation in contact with the free ends of the nanowhiskers. To assist in this, the catalytic particle melt, towards the end of the formation of the

20 nanowhisker, may have extra conductive substances injected into it, so as to improve the electrical contact with the bond pads.

Further specific components are set forth in the appended claims, and described below. In particular, these include a heterobipolar transistor, and light emitting diodes and photodetectors.

5   Light emitting diodes are well suited to the present invention, since it is possible to construct them with an emission wavelength which can be selected at will from a continuous range of wavelengths over the UV, visible, and infrared regions.

10   The present invention provides a light emitting diode, comprising a nanowhisker having a column of a diameter with a nanometer dimension, such as to exhibit quantum confinement effects,
the column comprising along its length in sequence first,
15   second and third semiconductor length segments comprising respectively an emitter, quantum well active segment and collector, said second segment having a different band gap from that of the first and second segments, and forming an active area of the light emitting diode.

20   One particular application of a light emitting diode is for emission of single photons. This is of use in various applications, but in particular in quantum cryptography, where unauthorised interception of a photon

stream will inevitably cause destruction or modification of the photon, in accordance with quantum theory, and thus corruption of the transmitted signal - see P. Michler, A. Imamoglu, M. D. Mason, P.J. Carson, G. F. Strouse, S. K. Buratto, Nature 406, 968 (2000); C. Santori, M. Pelton, G. Solomon, Y. Dale, Y. Yamamoto, Phys. Rev. Lett. 86, 1502 (2001).

The invention provides a single photon light source, comprising a one dimensional nanoelement, having disposed along its length a volume of optically active material sufficiently small to form a quantum well, with tunneling barriers formed on either side of the quantum well, such that in use the quantum well is capable of emitting a single photon at a time.

Another form of light source in accordance with the invention is designed for terahertz radiation, beyond the far infrared. Much work has been done on superlattices, pioneered by Capasso and co-workers at Lucent Technologies. Their 'quantum cascade' lasers utilise intersubband photon emission in InGaAs/InAlAs/InP heterostructures, and have achieved room temperature (pulsed mode) operation at wavelengths up to 17 microns. See for example IEEE Spectrum July 2002, pages

23,24,"Using Unusable Frequencies" and F. Capasso, C.
Gmachl, D. L. Sivco, and a. Y. Cho, "Quantum cascade
lasers" Physics Today, May 2000, pp. 34-39.

The invention provides a source of terahertz
5   radiation, comprising a nanowhisker having a column of a
diameter with a nanometer dimension, the column including
a multiplicity of layers of a first band gap
semiconductor interleaved with a multiplicity of layers
of a second band gap material, whereby to form a
10   superlattice, the dimensions being such that electrons
can move with a wave vector such as to radiate terahertz
radiation.

In components, structures and processes according to
the invention, an array of a large number of nanowhiskers
15   may be formed extending from a substrate, essentially
parallel to one another. There are various methods of
forming such arrays, for example positioning an array of
aerosol particles on the substrate to provide catalytic
seed particles, depositing particles on the substrate
20   from a colloidal solution, or forming on the substrate by
a nanoimprint lithography (NIL) process (or by any other
lithography process, e.g. e beam, UV, or X-ray), an array
of areas of predetermined shape (rectangular or other

- 21 -

shape) and thickness, which when heated, form balls of a desired volume to permit the nanowhisker growth process to proceed.

Such arrays may be employed as photonic crystals,

5   solar cells comprised of a large number of photodetectors, field emission displays (FED), converters to convert an infrared image to a visible light image, all as described herein below. A further application is that of a polarisation filter.

10   In processes of the invention, an array of a large number of nanowhiskers may be employed to create a layer of an epitaxial material on a wafer substrate of a cheaper substance, for example silicon. A long-standing problem in the art is the formation of single crystal

15   wafers of expensive III-V materials, from which chips can be formed. Much research has been made into forming single crystal layers on silicon wafer substrates – see for example WO 02/01648. However further improvements are desirable.

20   In accordance with the invention, a substrate of silicon or other substance is provided on which is grown a mask material, resistant to epitaxial growth, for example a dielectric material such as SiO_2, or Si_3N_4 . An

array of nanometer-dimensioned apertures is formed in the

mask material, such as by a NIL process, and catalytic

seed-forming material is deposited in the apertures.

Alternatively an array of seed forming material areas is

5   deposited on the substrate, and a layer of mask material

is then deposited over the substrate and the seed

particle areas. Application of heat causes melting of

the seed particle areas to create the seed particles, and

then growth of the nanowhiskers of the desired III-V or

10   other material is initiated. After growth of the

nanowhiskers, growth of the desired material continues,

using the whiskers as nucleation centres, until a single

continuous layer of the material is formed. The material

is single crystal epitaxial. As preferred, the seed

15   particle melt at the end of the nanowhiskers is removed

at a convenient opportunity to avoid contamination of the

epitaxial layer.

In a modification, mass growth of the epitaxial layer

is initiated, using the seed particle melts as nucleation

20   points, prior to formation of the nanowhiskers, and while

the growth underneath the seed particles is still in the

liquid phase.

In a further modification, microscopic V-grooves are formed in the upper surface of the silicon surface, for example <111> etchings in a <100> substrate. The seed particle forming areas are formed on the surfaces of the

5   V-grooves, whereby the nanowhiskers grow at an angle to the substrate, and cross one another at the grooves. This makes for a more efficient growth of the epitaxial layer from the nanowhisker nucleation centres. Further, grain boundaries between domain areas with different

10   growth phases are avoided; which has been a problem with prior processes.

     The present invention thus provides in a further aspect a method for forming an epitaxial layer of a desired material on a substrate of a different material,

15   the method comprising forming on a substrate a configuration of seed particle material areas, forming a layer of mask material around the seed particle areas, growing nanowhiskers from the seed particles areas of said desired material, and continuing to grow said

20   desired material, using the nanowhiskers as growth sites, whereby to create an epitaxial layer of said desired material extending over said substrate.

In a further aspect of the invention, processes have been developed for forming nanowhiskers of III-V material extending in the <100> direction, as opposed to the usual <111> direction for nanowhiskers. This has important

5   applications, particularly for nitride materials which tend to grow in the <111> direction, but with many stacking faults, as the material alternates between a zinc blende and wurtzite structure.

The invention provides a method of forming

10   nanowhiskers comprising providing a substrate, forming a configuration of seed particles on the upper surface, growing nanowhiskers from said seed particles which extend from the substrate initially in a <111> direction, and forming a short segment of a barrier material in said

15   nanowhiskers such as to change their direction of growth to a <100> direction.

In a further aspect, the invention provides method of forming nanowhiskers, a method of forming nanowhiskers, comprising providing a substrate, forming a configuration

20   of seed particles on the upper surface, growing nanowhiskers from said seed particles which extend from the substrate initially in a <111> direction, and changing the growth conditions of said nanowhiskers such

as to change their direction of growth to a <100> direction.

The present invention also relates to one-dimensional nanoelements incorporated in MEMS devices –

5   micromechanical devices.

In one aspect a substrate, for example of silicon, has a matrix of electrical contact areas formed on one surface. On each contact area, one, or a number, of nanowhiskers are formed from, for example, gold catalyst

10 particles so as to be upstanding from the substrate's surface. Each nanowhisker, or group of nanowhiskers may therefore be individually addressable by electrical signals. Such a structure may make contact with the end of a nerve or perhaps the nerves in the retina of an eye,

15 and the electrodes may be activated so as to provide a repairing or artificial function for enabling the nerve. Thus for example, when applied in the retina of an eye, the structure may overcome certain blindness problems.

In another aspect a nanowhisker is provided, which

20 may function as a nerve electrode or in other applications, wherein the whisker is formed of silicon or of a metal which may be oxidised, and the whisker is oxidised to form a layer of oxide along its length. The

particle melt at the end of the whisker however including

gold or other non- oxidisable material remains free of

oxide and may therefore be used to form an electrical

contact. This arrangement provides more precise

5   electrical characteristics than nanowhiskers with exposed

conductive material along their lengths and such

nanowhiskers may be used as nerve electrodes or as

devices where the capacitance of the nanowhisker is of

importance. As an alternative, other materials may be

10   used as the outer layer for example higher bandgap

shells, for example where the whisker is formed of

gallium arsenide, the outer layer may be gallium

phosphide.

       An important application of nanostructures is in

15   micromechanical cantilever beams where a beam fixed at

one end projects into space and may be subject to an

external force, for example, electrical or weight or an

external object or a chemical force, to give a bending of

the cantilever. This bending may be detected for example

20   by a change in electrical capacitance of the structure.

       In a further aspect the present invention provides

one or more nanowhiskers, which may or may not be

oxidised in accordance with the above-mentioned aspect of

the invention along their length to provide a cantilever or an array of cantilevers formed as a row or parallel beams. Such an arrangement may provide an order of magnitude or more sensitivity than a previous arrangement

5   where an etching process has been used to produce the beams.

One application for such cantilevers is where the whiskers are formed with a material with a coating which is sensitive to certain organic molecules or biological

10   molecules, such that a molecule, when making contact with a cantilever beam undergoes a certain chemical reaction. This produces certain stresses on the cantilever beam and causes bending of the beam, which may be detected by optical or electrical monitoring.

15   In a further specific aspect, a nanowhisker is formed on a substrate projecting up into an aperture of a layer of material, which is essentially insulative. The upper surface of the insulative layer has an electrically conductive material formed thereon. This electrically

20   conductive material is roughly the same height from the substrate as the tip of the nanowhisker, which has a conductive seed particle melt thereon. By appropriate activation of the conductive material, the whisker may be

made to mechanically vibrate within the aperture at a certain eigen frequency, for example, in the gigahertz range. During the period of a single vibration, a single electron is transferred from one side of the conductive

5   material to the other via the seed particle melt. This creates a current standard generator, where the current I through the conductive material is equal to product of the frequency of vibration and the charge e of an electron: $I = f \cdot e$.

10   If the whisker is sensitised to attract molecules of a certain type, then the deposition of a molecule onto the whisker will change the inertial characteristics of the whisker and therefore its natural frequency of vibration. This may therefore be detected by electrical

15   activation of the conductive material. This technique may be used to calculate the weight of a molecule to a very accurate degree.

BRIEF DESCRIPTION OF THE DRAWINGS

20   Preferred embodiments of the invention will be now be described merely by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic depiction of a fabrication technique according to the invention, for forming nanowhiskers: (a) deposition of size-selected Au aerosol particles onto a GaAs substrate; (b) AFM manipulation of the particles for the positioning of the whiskers; (c) alloying to make a eutectic melt between Au and Ga from the surface; (d) GaAs whisker growth.

Figure 2. (a) TEM micrograph of GaAs nano-whiskers grown from 10 nm Au aerosol particles. (b) SEM micrograph of a GaAs<111>B substrate with GaAs whiskers grown from 40 nm Au aerosol particles. (c) High-resolution electron microscope image 400 kV of GaAs whisker grown from an Au cluster. The inset shows a magnified part of the whisker.

Figure 3 is a schematic diagram of apparatus for carrying out the methods of this invention.

Figure 4. Composition profile of an InAs nanowhisker, according to an embodiment of the invention, containing several InP heterostructures, using reciprocal space analysis of lattice spacing. (a) High-resolution TEM image of a whisker with a diameter of 40 nm. (b) Power spectrum of the image in (a). (c) An inverse Fourier transform using the information closest to the InP part of the split 200 reflection. InP (bright) is

located in three bands with approximately 25, 8 and 1.5
nm width, respectively. (d) Superimposed images, using an
identical mask over the InP and InAs parts of the 200
reflection, respectively.

5   Figure 5. Analysis of InP heterostructures inside
InAs nanowhiskers. (a) TEM image of InP barriers (100,
25, 8, and 1.5 nm) inside a 40 nm diameter InAs
nanowhisker. (b) Magnification of the 8 nm barrier
region, showing crystalline perfection and the interface
10   abruptness on the level of monolayers. (c) Simulated
band-structure diagram of the InAs/InP heterostructures,
including (left edge) ideal formation of ohmic contacts
to InAs. (d) Ohmic I-V dependence for a homogeneous InAs
whisker , contrasted by the strongly nonlinear I-V
15   behavior seen for an InAs whisker containing an 80 nm InP
barrier . (e) Arrhenius plot showing measurements of
thermionic excitation of electrons across the InP barrier
(at a bias of 10 mV), yielding a barrier height of
0.57 eV.

20   Figure 6. Evaluation of transport mechanisms for
single barriers of various thick nesses, for use in
resonant tunneling diodes of the invention. (A) A SEM
image of a whisker on the growth substrate. (Scale bar

depicts 1 μm.) (B) An InAs/InP nanowhisker contacted by two alloyed ohmic contacts. (Scale bar depicts 2 μm.) (C) TEM image of an InAs whisker with an 8 nm InP segment perpendicular to the long axis of the whisker. (D) The

5   current-voltage characteristics for three different barrier situations;

Figure 7. High-resolution TEM imaging. (A) A TEM image of an InAs whisker grown in the <111> direction with two InP barriers for forming a first embodiment of

10   the invention. (Scale bar depicts 8 nm.) (B) A one-dimensionally integrated profile of the boxed area in A. The width of the barrier is about 5.5 nm (16 lattice spacing), and the interface sharpness is of the order of 1-3 lattice spacings, judged by the jump in image

15   contrast.

Figure 8. A resonant tunneling diode (RTD) forming an embodiment of the invention.

(A) TEM image of the top end of a whisker with the double barrier clearly visible, in this case with a

20   barrier thickness of about 5 nm (scale bar depicts 30 nm).

(B) The principle of the energy band diagram for the device investigated with the characteristic electronic states in the emitter region indicated (left).

(C) Current-voltage data for the same device as shown in A and B revealing a sharp peak in the characteristics, reflecting resonant tunneling into the ground state, E1z, with a voltage width of about 5 mV. This width can be translated into an energy width of the transition of about 2 meV, corresponding to the width of the shaded energy band in the emitter from which electrons tunnel. The device characteristics are shown in the inset, which provides a magnified view of the resonance peak for increasing voltage and for decreasing voltage .

Figure 9 is a schematic representation of the preferred embodiment of the resonant tunneling diode according to the invention;

Figure 10 is a schematic representation of a further embodiment of the invention including a wide band gap insulating segment;

Figure 11 is a schematic representation of a further embodiment of the invention comprising a hetero bipolar transistor (HBT);

Figure 12 is a band gap diagram of the HBT correlated with the HBT structure;

Figure 13 is a diagram showing band gap variation with compositional change of a ternary compound;

Figures 14A and 14B are diagrams showing band gap versus lattice dimensions for a variety of semiconductor compounds;

Figure 15 is a schematic representation of an embodiment of the invention comprising a light emitting diode and laser;

Figure 16 is a schematic representation of a further embodiment of the invention comprising the application of a laser to detection of individual molecules of desired species;

Figure 17 is a schematic representation of a further embodiment of the invention comprising the application of an array of lasers to patterning photoresists in a NIL process;

Figure 18A is a schematic representation of a further embodiment of the invention comprising a photodetector, and Figures 18B and 18C are variants thereof;

Figure 19A is a schematic representation of a further embodiment of the invention comprising a solar cell, and Figure 19B is a variant thereof;

Figure 20 is a schematic representation of a further embodiment of the invention comprising a radiation source of terahertz radiation;

Figures 21A-C are schematic representations for explaining an embodiment of the invention comprising a photonic crystal, and Figure 21D is a variant thereof for forming a 3-D photonics crystal;

Figures 22A-G are schematic representations of a further embodiment of the invention for forming a layer of material epitaxial with a substrate, wherein the lattices are not matched to one another;

Figures 23A-C are schematic representations for explaining a further embodiment of the invention for forming a layer of material epitaxial with a substrate, wherein the lattices are not matched to one another;

Figures 24A-B are schematic representations for explaining a further embodiment of the invention, for forming whiskers, which extend in a<100> direction, as opposed to the usual <111> direction;

Figures 25A-B are schematic representations of a further embodiment of the invention comprising a field emission display (fed), wherein the individual elements of the display are nanowhiskers and are individually

5   addressable;

Figure 26 is a schematic representation of a further embodiment of the invention comprising an arrangement for upconverting an image in the infrared region to a visible light region;

10   Figure 27 is a schematic representation of a further embodiment of the invention comprising an antenna for infrared radiation;

Figure 28 is a schematic representation of a further arrangement comprising a ferromagnetic whisker for

15   spintronics applications;

Figure 29 is a schematic view of a further embodiment of the invention comprising an array of selectively addressable electrodes for implantation into a nerve;

20   Figure 30 is a schematic view of a further embodiment of the invention comprising a nanowhisker with an oxidised outer surface along its length;

Figure 31 is a schematic view of a further embodiment comprising a row of nanowhiskers upstanding from a substrate and forming a cantilever arrangement;

Figure 32 is a schematic view of a further embodiment of the invention comprising a nanowhisker arranged for oscillation and providing precise measurements of weight and frequency; and

Figure 33 is a schematic view of a further embodiment of the invention, comprising the tip of a Scanning Tunneling Microscope.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Methods of producing nanowhiskers, in accordance with the invention will now be described. Such methods may be suitable for production of resonant tunneling diodes described below, and other electronic and/or photonic components, as will become apparent.

Whiskers are highly anisotropic structures, which are spatially catalyzed by molten metallic droplets, often unintentionally introduced as contaminants, on a crystal surface. Gold is commonly chosen as catalyst, or seed particle, since it forms eutectic alloys with semiconductor materials or constituents such as Si, Ga,

and In. The melting points of these eutectic alloys are
lower than the usual growth temperatures for Si and group
III-V materials. The molten metal droplet serves as a
miniature, liquid phase, epitaxy system, where precursors

5   are fed into it in the form of a vapour or, in this case,
by a molecular beam in vacuum. The growth is usually
referred to as vapour-liquid-solid growth. The
electrical and optical properties of semiconductor
nanowhiskers are fundamentally determined by their

10   crystalline structure, shape, and size. In particular, a
small variation of the width of the whisker provokes a
considerable change in the separation of the energy
states due to the quantum confinement effect.
Accordingly, it is of importance that the whisker width

15   can be chosen freely, and, of equal importance, is that
the width can be kept constant for extended whisker
lengths. This, together with the possibility of
positioning whiskers at selected positions on a
substrate, is necessary for an integration of whisker

20   technology with current semiconductor component
technology.

        According to the invention, techniques have been
developed for the synthesis of size-selected, epitaxial

nanowhiskers, grown on a crystalline substrate. The
Chemical Beam Epitaxy apparatus employed in the
techniques described below is shown schematically in
Figure 3.

5   Chemical Beam Epitaxy (CBE) combines a beam epitaxial
technique like Molecular Beam Epitaxy (MBE) and the use
of chemical sources similar to Metal Organic Chemical
Vapor Deposition (MOCVD). In MOCVD or related laser
ablation techniques, the pressure inside the reactor is
10   usually greater than 10 mbar and the gaseous reactants
are viscous, which means that they have a relatively high
resistance to flow. The chemicals reach the substrate
surface by diffusion. CBE reduces the pressure to less
than 10^{-4} mbar and the mean free path of the diffusants
15   then becomes longer than the distance between the source
inlet and the substrate. The transport becomes collision
free and occurs in the form of a molecular beam. The
exclusion of the gas diffusion in the CBE system means a
fast response in the flow at the substrate surface and
20   this makes it possible to grow atomically abrupt
interfaces.

The CBE apparatus shown in Figure 3 consists of a
UHV (ultra-high vacuum) growth chamber 1001 where the

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sample 1021 is mounted on a metal sample holder 1041
connected to a heater 1061. Around the chamber there is
a ring 1081 filled with liquid nitrogen that is called
the cryoshroud. The cryoshroud pumps away species that
5   don't impinge or that desorb from the substrate surface.
It prevents contamination of the growing surface layer
and reduces the memory effect. Vacuum pumps 1101 are
provided.

The sources 1121 for CBE are in liquid phase and
10   they are contained in bottles which have an overpressure
compared to the chamber. The sources are usually as
follows: TMGa, TEGa, TMIn, TBAs, TBP. The bottles are
stored in constant-temperature baths and by controlling
the temperature of the liquid source, the partial
15   pressure of the vapor above the liquid is regulated. The
vapor is then fed into the chamber through a pipe complex
1141 to, in the end of the pipe just before the growth
chamber, a source injector 1161. The source injector is
responsible for injection of the gas sources into the
20   growth chamber 1001, and for generation of a molecular
beam with stable and uniform intensity. The III-
material, from the metal organic compounds TMIn
(trimethylindium), TMGa (trimethylgallium) or TEGa

(triethylgallium), will be injected by low temperature

injectors to avoid condensation of the growth species.

They will decompose at the substrate surface. The V-

material is provided by the metal-organic compounds, TBAs

5   (tertiarybutylarsine) or TBP (tertiarybutylphosphine). As

opposed to the decomposition of the III-material, the

V-material will be decomposed before injection into the

growth chamber 1001, at high temperatures, in the

injectors 1161. Those injectors 1161 are called cracking

10   cells and the temperatures are kept around 900°C. The

source beam impinges directly on the heated substrate

surface. Either the molecule gets enough thermal energy

from the surface substrate to dissociate in all its three

alkyl radicals, leaving the elemental group III atom on

15   the surface, or the molecule get desorbed in an

undissociated or partially dissociated shape. Which of

these processes dominates depends on the temperature of

the substrate and the arrival rate of the molecules to

the surface. At higher temperatures, the growth rate will

20   be limited by the supply and at lower temperatures it

will be limited by the alkyl desorption that will block

sites.

This Chemical Beam Epitaxy method permits formation

of heterojunctions within a nanowhisker, which are abrupt, in the sense there is a rapid transition from one material to another over a few atomic layers.

For the purposes of this specification, "atomically abrupt heterojunction", is intended to mean a transition from one material to another material over two or less atomic monolayers, wherein the one material is at least 90% pure on one side of the two monolayers, and the other material is at least 90% pure on the other side of the two monolayers. Such "atomically abrupt heterojunctions" are sufficiently abrupt to permit fabrication of heterojunctions defining quantum wells in an electrical component having a series of heterojunctions and associated quantum wells.

For the purposes of this specification, "sharp heterojunction", is intended to mean a transition from one material to another material over five or less atomic monolayers, wherein the one material is at least 90% pure on one side of the five monolayers, and the other material is at least 90% pure on the other side of the five monolayers. Such "sharp heterojunctions" are sufficiently sharp to permit fabrication of electrical components having one, or a series of, heterojunctions

within a nanoelement, where the heterojunctions have to

be accurately defined. Such "sharp heterojunctions" are

also sufficiently sharp for many components relying on

quantum effects.

5   As an illustration, in a compound AB used in the

nanowhiskers of the invention, where A represents one or

more selected elements of a first group and B represents

one or more selected elements of a second group, the

total proportions of the selected element(s) in the first

10   group and the selected element(s) in the second group are

predetermined to constitute a semiconductor compound

designed to provide desired properties. The compound AB

is considered 90 % pure when the total proportion of the

selected element(s) within each group is at least 90 % of

15   its predetermined proportion.

Example 1

Figures 1 and 3 show whiskers of predetermined sizes

grown from several III-V materials, in particular, GaAs

whiskers with widths between 10 and 50 nm. These

20   whiskers can be grown rod shaped with a uniform diameter,

in contrast to earlier reports on epitaxially grown nano-

whiskers, which tended to be tapered, narrowing from the

base towards the top. As catalysts, size-selected gold

aerosol particles were used, whereby the surface coverage

can be varied independently of the whisker diameter.

The whisker width in general is slightly larger than

the seed particle diameter. This is mainly due to two

5   factors: First, the gold particle incorporates Ga and

possibly As from the substrate, which makes the particle

grow. Second, when the particle melts, the base diameter

of the liquid cap will be determined by the wetting angle

between the alloy and the substrate surface. Simple

10   assumptions give a widening of up to 50%, depending on

temperature and particle diameter, and introduce a

reproducible correlation between the particle diameter

and the width of the whisker.

A GaAs<111>B substrate 10 was used, etched in

15   HCL:H_2O, 1:10 to remove any native oxide and surface

contaminants before aerosol deposition. The size-

selected Au particles 12 were made in a locally

constructed aerosol facility situated in a glove box 14

with ultra pure N_2 atmosphere. The particles are created

20   in a tube furnace 16 by the evaporation/condensation

method, at a temperature of about 1750°C, and are

electrically charged by UV light at 18. The particles

are size selected by means of a differential mobility

analyzer DMA 20. The DMA classifies the sizes of charged

aerosol particles by balancing their air resistance

against their mobility in an electric field. After size

classification, the particles were heated to 600°C, in

5   order to make them compact and spherical. The setup

gives an aerosol flow with a narrow size distribution,

the standard deviation being <5% of the mean particle

diameter. Still charged, the particles were deposited on

the substrate 10 by means of an electric field E. Size-

10   selected aerosol particles in the range between 10 and

50 nm were used to grow whiskers.

After aerosol deposition, some samples were

transferred to an AFM Topometrix Explorer 24, also

situated inside the glove box, and connected to the

15   aerosol fabrication equipment. Thus, these samples were

exposed only to sub-ppm levels of H_2O and O_2 during the

deposition and manipulation phases. With the AFM tip,

specific particles 12 were selected and placed in a

predetermined configuration, giving complete control of

20   the positioning of individual seed particles.

The GaAs substrate 10 with Au aerosol particles 12,

either arranged or as deposited, was then transferred

into a chemical beam epitaxy CBE chamber. In a CBE

configuration, GaAs growth occurs under vacuum/molecular
beam conditions and with metal organic sources, in this
case, triethylgallium TEG and tertiarybutylarsine TBA.
The TBA is thermally pre-cracked to predominantly As_2

5   molecules, while the TEG usually cracks after impinging
on the surface of the substrate. The growth is typically
performed with a slight As_2 over-pressure, which means
that the Ga flow determines the growth rate. Just before
growth, the substrate was heated by a heater to 600°C for

10   5 min, while exposed to an As_2 beam. In this step, the Au
droplet can form an alloy with the GaAs constituents,
whereby the Au particle absorbs some of the Ga from the
substrate. The Au/Ga alloy forms at 339°C. However, this
step also works as a deoxidizing step, taking away any

15   new native oxide layer, originating from the transport to
and from the glove box system. The oxide is expected to
evaporate at 590°C, although this is not always the case.
The volatility of the oxide can be followed with
reflective high-energy electron diffraction RHEED. With

20   a successful transfer, a streaky diffraction pattern,
indicating a crystalline, reconstructed surface, can be
seen already at temperatures lower than 500°C. Often,
however, the oxide stays stable up to 590°C, sometimes as

high as 630°C. The whisker growth was performed at

substrate temperatures between 500 and 560°C, with a TEG

pressure of 0.5 mbar and a TBA pressure of 2.0 mbar.

After growth, the samples were studied by scanning and

5   transmission electron microscopy SEM and TEM.

The resulting whiskers were rod shaped and fairly

homogeneous in size, although their lengths varied

slightly. The size homogeneity was clearly dependent on

the volatility of the surface oxide. For samples with a

10   hard oxide, as seen with RHEED, the size homogeneity was

decreased. An oxygen-free environment is therefore to be

preferred for reproducible results. At the growth

temperatures described, no tapering of the whiskers was

observed, irrespective of particle size. For whiskers

15   grown below 500°C, however, there were clear signs of

tapering. The growth of either rod-shaped or tapered

whiskers, depending on temperature, is explained by the

absence or presence of uncatalyzed growth on the surfaces

parallel to the long axis of the whisker. The simplest

20   surfaces of this orientation are <110> facets. Under

ordinary CBE growth conditions, close to the ones used in

these experiments, <110> facets are migration surfaces.

However, at lower temperature, the Ga diffusion constant

decreases, which initiates growth on the <110> facets. In MOCVD growth the Ga migration length is even smaller, which explains the typically tapered whiskers of prior workers.

5   In Fig. 2a, a TEM image of a truss of 10±2-nm-wide whiskers grown from 10 nm particles is shown. The relatively low density of whiskers is illuminated by the SEM image in Fig. 2b, which is of a GaAs<111>B substrate with GaAs whiskers grown from 40 nm Au aerosol particles.

10   In Fig. 2c, a single 40-nm-wide whisker is shown in a high-resolution TEM micrograph. The growth direction is perpendicular to the close-packed planes, i.e., 111 in the cubic sphalerite structure, as found by other groups. Twinning defects and stacking faults can also be

15   observed, where the whisker alternates between cubic and hexagonal structure. Most of the whisker has the anomalous wurzite structure W, except for the part closest to the Au catalyst, which always is zinc blende Z. SF = stacking fault, T=twin plane. The change in

20   image contrast at the core is due to the hexagonal cross-section.

       Such a growth method is used in the method described below with reference to Figures 4 to 6 for forming

whiskers with segments of the whisker with different compositions. The method is illustrated by InAs whiskers containing segments of InP.

Example 2

5   Conditions for growth of nanowhiskers allow the formation of abrupt interfaces and heterostructure barriers of thickness from a few monolayers to 100s of nanometers, thus creating a one-dimensional landscape along which the electrons move. The crystalline

10   perfection, the quality of the interfaces, and the variation in the lattice constant are demonstrated by high-resolution transmission electron microscopy, and the conduction band off-set of 0.6 eV is deduced from the current due to thermal excitation of electrons over an

15   InP barrier.

In this method, the III-V whiskers are grown by the vapor-liquid-solid growth mode, with a gold nanoparticle catalytically inducing growth, in the manner described above. Growth occurs in an ultrahigh vacuum chamber 100,

20   Figure 3, designed for chemical beam epitaxy (CBE). The rapid alteration of the composition is controlled by the supply of precursor atoms into the eutectic melt, supplied as molecular beams into the ultrahigh vacuum

chamber. The rapid switching between different
compositions (e.g., between InAs and InP) is obtained via
a sequence where growth is interrupted as the indium
source (TMIn) is switched off, followed by a change of

5   the group III sources. Finally, the supersaturation
conditions, as a prerequisite for reinitiation of growth,
are reestablished as the indium source is again injected
into the growth chamber.

For the abruptness of the interfaces, Figure 4 shows

10 TEM analysis of an InAs whisker containing several InP
heterostructure barriers. In Figure 4a, a high-
resolution image of the three topmost barriers is shown,
recorded with a 400 kV HRTEM (point resolution 0.16 nm).
Figure 4b shows a nonquadratic power spectrum of the HREM

15 image, showing that the growth direction is along [001]
of the cubic lattice. The reflections show a slight
splitting due to the difference in lattice constants
between InAs and InP. Figure 4c shows an inverse Fourier
transform, using a soft-edge mask over the part of the

20 200 reflection arising from the InP lattice. A
corresponding mask was put over the InAs part of the
reflection. The two images were superimposed as in
Figure 4d.

Figure 5a shows a TEM image of an InAs/InP whisker.

The magnification of the 5 nm barrier in Figure 5b shows

the atomic perfection and abruptness of the

heterostructure interface. Aligned with the 100 nm thick

5   InP barrier, the result of a 1D Poisson simulation

(neglecting lateral quantization, the contribution of

which is only about 10 meV) of the heterostructure 1D

energy landscape expected to be experienced by electrons

moving along the whisker is drawn (Figure 5c). This

10   gives an expected band offset (q¼B) in the conduction

band (where the electrons move in n-type material) of 0.6

eV. This steeplechase-like potential structure is very

different from the situation encountered for electrons in

a homogeneous InAs whisker, for which ohmic behavior

15   (i.e., a linear dependence of the current (I) on voltage

(V)) is expected and indeed observed (indicated curve in

Figure 5d). This linear behavior is dramatically

contrasted by the indicated I-V curve measured for an

InAs whisker containing an 80 nm thick InP barrier.

20   Strongly nonlinear behavior is observed, with a voltage

bias of more than 1V required to induce current through

the whisker. This field-induced tunnel current increases

steeply with increasing bias voltage, as the effective

barrier through which the electrons must tunnel narrows.
To test whether the ideal heterostructure band diagram
within the 1D whisker is valid, the temperature
dependence of the current of electrons overcoming the InP
5   barrier via thermionic excitation was measured. The
result is shown in Figure 5e, where the logarithm of the
current (divided by T^2) is plotted as a function of the
inverse of the temperature in an Arrhenius fashion,
measured at a small bias voltage (V) 10 mV) to minimize
10   band-bending effects and the tunneling processes
described above. From the slope of the line fitted to the
experimental data points an effective barrier height,
q¼B, of 0.57 eV may be deduced, in good agreement with
the simulation.
15   An added benefit of this approach to realizing
heterostructures within 1D whiskers is the advantageous
condition for combining highly mismatched materials,
provided by the efficient strain relaxation by the
proximity to the open side surface in the whisker
20   geometry. In comparison, only a few atomic layers may be
epitaxially grown in transitions between materials like
InAs and InP with different lattice constants before

either islanding or misfit dislocations occur, thereby

preventing formation of ideal heterointerfaces.

Resonant Tunneling Diodes and Heterobipolar Transistors

        The present invention also comprises, at least in

preferred embodiments, functional 1D (one-dimensional)

resonant tunneling diodes (RTDs) obtained via bottom-up

assembly of designed segments of different semiconductor

materials in III/V nanowires. Such RTDs comprise, in

order, an emitter segment, a first barrier segment, a

quantum well segment, a second barrier segment, and a

collector segment. As is known to those skilled in the

art, the barrier segments in RTDs are made thin enough

that significant quantum tunneling of charge carriers is

possible under conditions that favor such tunneling. In

RTDs according to the invention, fabricated in

nanowitres, the nanowhiskers may be made thin enough so

that the central quantum well is effectively a quantum

dot.. In a concrete example, the emitter, collector and

the central quantum dot may be made from InAs and the

barrier material from InP. In an example, excellent

resonant tunneling behavior, with peak-to-valley ratios

of up to 50:1, was observed.

According to the invention 1D heterostructure devices were fabricated utilizing semiconductor nanowhiskers. The whiskers were grown by a vapor-liquid-solid growth mode, size controlled by, and seeded from,

5   Au aerosol particles, as more fully described above in Examples 1 and 2. Growth takes place in a chemical beam epitaxy chamber under ultra-high-vacuum conditions where the supersaturation of the eutectic melt between the Au particles and the reactants acts as the driving force for

10   whisker growth.

The incorporation of heterostructure segments into the whiskers is achieved via the following switching sequence (more fully described above); the group III-source beam is switched off to stop growth, and

15   shortly thereafter the group V-source is changed. Once the group III-source is reintroduced into the chamber, the supersaturation is re-established and growth continues. In examples described below the material system used was InAs for the emitter, collector and dot,

20   and InP as the barrier material. The aerosol particles were chosen so that the final whisker diameter was 40-50 nm. In order to prepare contacted electronic devices with single nanowhiskers as the active elements, the

whiskers were transferred from the growth substrate to a
SiO_2-capped silicon wafer, on top of which large bond pads
were predefined by Au metal evaporation through a
transmission electron microscope (TEM) grid mask. In

5   Fig. 6B a scanning electron microscope (SEM) image of a
nanowire device is shown, displaying the alignment
capability in the e-beam lithography system, allowing
positioning of metallic electrodes on the nanowires with
an accuracy that is better than 100 nm. Figure 6D shows

10   the current-voltage (I-V) characteristics of a set of
single-barrier devices, as the thickness of the InP
barrier was varied from 80 nm down to zero. The thicker
InP segments act as ideal tunneling barriers for electron
transport, allowing only thermal excitation over this

15   barrier (measured to be about 0.6 eV (23)) or tunneling
made possible by the effective thinning of the barrier
when a large bias is applied to the sample. In Fig.6D it
can be seen that almost no current flows through the
thick InP barrier. In samples containing thinner single

20   barriers (Fig. 2C), quantum tunneling is possible and
electrons can penetrate barriers thinner than about 10 nm
in thickness. In the extreme case with zero barrier
thickness, the I-V characteristics are perfectly linear

down to at least 4.2 K.   In order to verify the

crystalline quality and to evaluate the abruptness of the

heterointerfaces high-resolution TEM investigations were

performed.   In Fig. 7A a magnification of a 5.5 nm thick

5   InP barrier in a <111>-InAs nanowhisker is shown, where

the (111) lattice planes can be clearly seen.   From the

integrated profile of the area in Fig. 7A the sharpness

of the interfaces was determined to be 1-3 lattice

spacings.   The average spacing between the lattice

10   fringes in the lighter band is 0.344 nm, corresponding

well to d111= 0.338 nm of InP.   Figure 7B is a one-

dimensionally integrated profile of the boxed area in A.

The width of the barrier is about 5.5 nm (16 lattice

spacings), and the interface sharpness is of the order of

15   1-3 lattice spacings, judged by the jump in image

contrast.   The background is not linear due to bend and

strain contrast around the interfaces.   The difference in

lattice spacing between the InP and the InAs is 3.4%,

which corresponds well with the theoretical value of the

20   lattice mismatch (3.3%).

Since the heterointerfaces were determined to be

abrupt enough for making high quality quantum devices,

double-barrier resonant tunneling devices may therefore

be envisaged. A barrier thickness of about 5 nm was

chosen. In Fig. 8A a TEM image of such a double barrier

device structure formed inside a 40 nm wide nanowhisker

can be seen. The barrier thickness is roughly 5 nm on

5   either side of the 15 nm thick InAs quantum dot. Below

the TEM image (Fig. 8B) the energy band diagram expected

for the device is shown, with the longitudinal

confinement (z-direction) determined by the length of the

dot and the lateral confinement (perpendicular direction)

10   depending on the diameter of the whisker. For this

device only the lowest transverse quantized level was

occupied (splitting of the order of 5 meV), with the

Fermi energy indicated, determining the highest occupied

longitudinal states filled with electrons. In between the

15   two InP barriers the fully quantized levels of the

central quantum dot are indicated, with the same sequence

as schematically indicated in the emitter region for the

transverse quantised levels, but with a greater splitting

(of the order of 100 meV) between the longitudinal

20   quantized states in the quantum dot and an approximate

quantization energy for the ground state of $E_{1z}=40$ meV.

At zero applied bias, the current should be zero since no

electronic states in the emitter are aligned with any

states in the central dot because of the difference in

energy quantization between the dot and the emitter. As

the bias is increased the states in the dot will move

towards lower energy and, as soon as the lowest dot-state

5   is aligned with the Fermi level, the current starts to

increase (here the Fermi level is assumed to lie between

the two lowest states in the emitter). When the dot-

state falls below the energy level of the first emitter

state the current again drops to zero, resulting in the

10   characteristic negative differential resistance.

    The electrical properties of this 1D DBRT device are

presented in Fig. 8C, showing almost ideal I-V

characteristics, as expected for such a device. The I-V

trace shows no current below a bias of around 70 mV,

15   corresponding to the bias condition for which electrons

must penetrate both barriers plus the central InAs

segment to move from the emitter to the collector. At a

bias of about 80 mV a sharp peak is seen in the I-V

characteristics, with a half-width of about 5 mV in bias

20   (which can be translated into an energy sharpness of the

resonance of about 1-2 meV). The peak-to-valley ratio of

the 80 mV peak is extremely high, about 50:1, and was

seen in different samples investigated. After the deep

valley, the current increases again for a bias of about 100 mV, with some unresolved shoulder features observed on the rising slope. Note that the I-V trace for increasing bias voltage coincides with that for

5   decreasing bias voltage indicating that the device characteristics are highly reproducible and exhibit negligible hysteresis effects. In addition, the 80 mV appears similarly in the reverse bias polarity. In this case the peak is only slightly shifted (5 mV) suggesting

10 a high symmetry of the device structure. Accordingly, these results report the investigation of the materials and barrier properties of single heterostructure barriers inside semiconductor nanowires, bridging the gap from thick barriers, for which only thermal excitation above

15 the barrier is possible, down to single barrier thickness, for which tunneling through the barrier dominates.

With this approach one-dimensional, double-barrier resonant tunneling devices have been prepared, with

20 high-quality device properties, and an energy sharpness of about 1 meV and peak-to-valley current ratio of 50:1.

Referring now to Figure 9, a preferred embodiment of a resonant tunneling diode is shown, having a nanowhisker

40 extending between collector and emitter contacts 42,

44, 2 microns apart. First and second InAs portions 46,

48 of the whisker make electrical contact with respective

contacts 42, 44. Barrier portions 50,52 of InP separate

5   a central quantum dot or quantum well portion of InAs,

54, from the emitter and collector portions. The length

of the portion 54 is around 30 nm. The precise

dimensions will be selected in dependence upon bandgap

barrier height, etc., in order to achieve appropriate

10   quantum confinement.

The diode operates in the conventional way of RTDs;

for an explanation of the theory of operation; see, for

example, Ferry and Goldnick, Transport in Nanostructures,

CUP 1999, pp 94 et seq.

15   In the RTD of Figure 9, the segments 50, 52 may be

replaced by a wide band gap insulating material, in the

manner shown in Figure 10. Referring to Figure 10, an

embodiment is shown having an insulating segment. A

germanium whisker 100 is grown by the processes described

20   above, having a short segment 102 of silicon. Lattice

mismatch is accommodated by radial outward expansion of

the whisker. This silicon dot is oxidised by heat to

give a large silicon dioxide spacer 104 within the

germanium whisker. This has an extremely stable large

bandgap offset. Aluminium can be used instead of silicon.

This embodiment can be used for example for tunneling

effects, in the embodiment of Figure 9.

5   As regards making electrical contacts with the

collector and emitter portions of the embodiment of

Figure 9, this can be done in different ways. The

whisker may be positioned across large metallised bond

pads, as shown in Figure 9. Alternatively, the

10   nanowhisker may be positioned on a substrate, its

position identified by a suitable scanning method, and

then bond pads may be formed over the ends of the whisker

by a metallization process. Another alternative is to

leave the nanowhisker extending from the substrate, where

15   it makes contact at its base with an electrical contact,

to encapsulate the whisker in a resin or glassy

substance, and then form an electrode over the

encapsulation, making electrical contact with the whisker

tip. This latter method may be more suitable for

20   integration with other electrical components and

circuits.

Referring now to Figures 11 to 14, an embodiment of

the invention is disclosed which comprises a

heterojunction bipolar transistor (heterobipolar

transistor; HBT); this differs from the conventional

bipolar transistor in that different band gap materials

are used in the transistor. For example, a nanowhisker

5   110 may have an emitter segment 112 of GaP, connected to

a base segment 114 of p-doped Si, which is in turn

connected to an n-doped collector segment 116 of Si.

Metallisation electrodes 118 make contact with the

respective segments 112, 114, and 116. Figure 12 shows a

10   band gap diagram for the HBT. By reason of the

relatively wide band gap of the emitter, minority current

flow from the base to the emitter is inhibited. The

depletion area between the base and collector is

characterized by a gradual change in doping from p-type

15   to n-type. As an alternative, the base and collector may

be formed of ternary or quaternary materials, being a

stoichiometric composition, and the composition gradually

changes over a large number of lattice planes, say 100 to

1000, to give the required depletion region field.

20   Change in energy band gap with composition is shown in

Figure 13 for the ternary mixture $Al_xGa_{1-x}As$.

Figure 14 shows variation in bandgap energy and

lattice parameters for a variety of III-V materials. It

will be appreciated that with the method of forming

nanowhiskers according to the invention, it is possible

to form heteroepitaxial junctions of materials with

widely different lattice parameters, e.g. GaN/AlP, the

5   lattice mismatch being accommodated by radial bulging of

the whisker.

Photonics Components

Referring to Figure 15, this shows schematically an

extremely small LED capable of single photon emission.

10   Single photon emission is of importance, for example for

quantum photography or detection of individual molecules

of molecular species. A whisker 150 has anode and

cathode outer regions 152 of indium phosphide either side

of an inner region 156 formed of indium arsenide, so as

15   to define a quantum well. Regions 152 are connected to

respective anode and cathode electrical contacts, formed

as metallisation areas 158. In contrast to planar

devices, where because of the need for lattice matching

and for relieving mismatch strain, only certain

20   wavelengths are possible, an important point of this

embodiment is that the wavelength of the LED is fully

variable since the materials making up the diode may be

of any desired composition to achieve a desired

wavelength of emission (see Figure 14 discussed above),

since lattice mismatch is accommodate by radial outward

bulging of the whisker. Since the materials may be

stoichiometric compositions, the wavelength is

5   continuously variable across the range from 1.5ev to

0.35ev. A one-dimensional structure requires much less

processing than prior art layered structures and is made

by a self-assembly process, with the whole structure

between the electrical contacts. If a laser construction

10   is required, Fabry Perot (FP) cleavage planes 159 are

formed spaced an appropriate distance apart. As an

alternative, regions 159 are formed as mirrors comprising

superlattices. The superlattices may be formed as

alternating sequences of InP/InAs, the sequence

15   alternating over segments of only a few lattice planes,

as is known to those skilled in the art.

LEDs, lasers, and other micro cavity structures are

often fabricated with gallium nitride (GaN). Whilst

nitrides have a number of advantages, particularly in

20   optics, problems with nitrides are that firstly they are

filled with dislocations and that secondly there is a

lack of suitable substrates (sapphire being one commonly

used substrate). Whiskers can be made with defect-free

nitrides, and there is not a problem of lattice matching to a substrate. A regular FP laser can be made, with the structure of Figure 15, with dimensions less than 300nm, preferably of the order of 100nm. It is a bottom up

5   structure, which is well suited to reading DVDs and writing thereto. Nitride systems are quite well suited for whisker growth.

The light source-emitting region 156 can be made as small as about $20nm^3$. This represents an extreme example

10   of a point source and can be used, as indicated schematically in Figure 16 to locally excite individual biological cells 160. The light source 156 provides a near field 162 (exponentially decaying) which excites the cell 160 since the physical spacing between the light

15   source and object is a fraction of a wavelength. It is of use in DNA sequencing, and, as shown, the source 156 may be mounted in a groove 164 of a glass capillary tube 166. The cell flows along the tube as part of a fluid mixture, and flows past the source 156.

20   Referring to Figure 17, this shows an embodiment of the invention adapted for Nano Imprint Lithography (NIL), where an array 170 of whiskers 156, providing point sources of light, are individually addressable by an

energisation source 172. The array is mounted on a

carriage 174 movable over the surface of a resist

material 176. The carriage is movable in steps of 20nm,

and at each step, the whiskers 156 are selectively

5   energised in order to illuminate the material 176 with

near field light, and to create a desired developable

pattern in the resist 176.

Referring to Figure 18A, a photodetector is shown in

accordance with the invention. For example, a

10   nanowhisker 180 may extend between metallised contact

pads 182. There is typically a high contact resistance,

between 10KO to 100KO, arising from small contact areas

between pads182, and whisker 180. The whisker may

comprise an n-doped indium phosphide portion 184, and a

15   p-doped indium phosphide portion 186, with a p-n junction

188 between, which may be abrupt, or may extend over a

large number of lattice planes. This arrangement is

suitable for detecting light with wavelengths 1.3 micron

or 1.55 microns. As indicated in Figure 14, any desired

20   compositional "match" may be used, and therefore the

materials can be modified for detection of any

wavelength, from 1.55 microns or less. As an

alternative, a PIN or Schottky diode structure may be

used. A PIN structure, as shown in Figure 18B has an intrinsic semiconductor material segment 188 between the two semiconductor portions 184 and 186. The whisker is constructed as described with reference to Figure 10. A

5   Schottky diode structure, as shown in Figure 18C has a base portion 189 formed as a metallisation contact from which the whisker extends; the interface between the contact and the whisker forms the Schottky diode. The lower frequency limit on detection of radiation is in the

10   terahertz region of the electromagnetic spectrum.

Referring to Figure 19A, a solar cell application is shown for the photodetector structures of Figure 18. Millions of whiskers 190, each having p- and n-doped portions 191, 192 are formed on a substrate 193, doped

15   (P+). The whiskers are formed by growth using gold, or other, nanoparticles, deposited onto substrate 193, e.g., from an aerosol. The whiskers may be encapsulated in plastics 194 and have a transparent tin oxide electrode 196 on the upper surface, which makes contact with the

20   free ends of the whiskers to permit electrical current to flow along the length of the whiskers. The structure is extremely efficient in trapping light since each whisker is 100% reliable. The overall efficiency is between 35

and 50% and is of use in multi-bandgap solar cells. By contrast amorphous silicon grown at 300°C gives an efficiency of about 10%. Crystalline silicon gives an efficiency of about 15% and special purpose III-V solar

5   cells for space applications are grown at 400°C and have an efficiency of up to 25%. Grätzel solar cells for space applications have titanium dioxide nanoparticles painted on solar panels, with an appropriate dye; such cells have an efficiency up to about 8%.

10   Referring to the modification shown in Figure 19B, each whisker of the solar cell array is modified to the form shown 197, with different segments of different materials 198 along its length. These materials are selected so that the p-n junctions absorb light at

15   different wavelengths. The point along the whisker at which the whisker is most sensitive to light of a particular wavelength depends on the precise structure of the solar cell and factors such as reflection and refraction within the structure.

20   The embodiment of Figures 19A-B is inexpensive, since the growth conditions are inexpensive, and further only very small quantities of expensive materials are required. In alternative constructions, the whiskers can

be silicon (least expensive) or germanium.   The length of
the whiskers is 1 or 2 microns. A PN junction is achieved
by doping the whisker along part of its length, or by
forming Schottky barriers, as indicated in Figure 18C at
5   the base of the whisker.

        Referring to Figure 20, an embodiment is shown,
which is a source of very long wavelength infrared
radiation, e.g., at terahertz frequencies.   An indium
phosphide nanowhisker 200 has a series of very thin
10   indium arsenide stripes 202, separated by spacer stripes
204 of indium phosphide.   The stripes are grown by the
process described above.   Each stripe 202, 204 is a few
lattice planes wide, and the stripes create a
superlattice 206.   By applying a voltage across electrode
15   contacts 208, electrons move across the superlattice.
The superlattice creates a series of quantum well
bandgaps (potential wells) which, according to the Bloch
theorem will give a conduction band with allowable
regions of electron wave number or momentum k -these
20   allowable regions correspond to terahertz frequencies,
thereby to create terahertz emission.

        Figures 21A-21D illustrate an embodiment of the
invention, implemented as a photonic crystal.   Photonic

crystals are well known - see for example copending

application WO 01/77726. In the main, prior methods of

forming photonic crystals involve etching air holes in a

substrate according to a predetermined lattice pattern.

5   A concept of this embodiment is to use a patterning

technique for defining a crystal lattice pattern on a

substrate, but to grow nanowhiskers to define the

crystal, rather than etching holes. This has numerous

advantages in that etching techniques are not as reliable

10   (etching harms the substrate surface) as a bottom up

technique of growing whiskers. Therefore the whisker

technique is more accurate and gives higher quality; and

simplicity, as well as economy in that fewer process

steps are required.

15   Referring to Figure 21A, a substrate 210 has a

triangular lattice pattern of square patches 212 of gold

about $300nm^2$, spaced apart by a distance of 300nm, the

patches having been formed by ebeam lithography, UV

lithography or a nanoimprint lithography (NIL) process.

20   The substrate is initially prepared before gold

deposition as a clean substrate without oxide

contaminants. The substrate is heated to melt the gold

rectangles so that they form balls 214, about 100nm

diameter, as shown in Figure 21B, which are then

annealed. Whiskers 216 are then grown by the process as

described in Example 1, about 100nm wide to form a

photonics crystal, as shown in Figure 21C.

5   It is possible in accordance with the invention to

define three-dimensional photonic crystals by whisker

formation. This can be done as indicated in Figure 21D

by forming each whisker with a sequence of segments 217,

218 of different materials, for example an alternating

10   sequence of III-V materials such as InAs/GaAs, or group

IV materials such as Ge/Si, in accordance with the method

of Example 2, so that at intervals along each whisker,

segments are provided with an appropriate refractive

index to form a photonic band gap.

15   Single Crystal layers of III-V Materials

Referring to Figures 22A-22G, an embodiment of the

invention is shown for growing epitaxial layers of a

desired material on a substrate. As shown in Figure 22A

& B, a silicon or gallium arsenide substrate 220 has

20   formed on an upper surface rectangles 222 of gold, indium

or gallium, which are positioned on the substrate by a

stamp 223 in a NIL process or as described in Example 1.

An epitaxial mask deposit 224 a few nanometers wide of

dielectric material, for example, silicon dioxide or silicon nitride, are formed over the substrate 220 and around rectangles 222. Heat is applied to anneal the rectangle to balls 226, Figure 22C, and whiskers 228,

5   Figure 22D, are grown of for example InP or GaAs. Alternatively a carbon-based material is used as the deposit 224 (a carbon based material stabilises the particle when the ball is formed by annealing, the dielectric material being desorbed). The balls are used

10   as seed openings for bulk growth i.e. a layer of the desired material. The dielectric layer prevents atomic bonding and lattice mismatch effect between the substrate and the crystal layer. The whiskers grow together with a bulk layer of InP or GaAs 229, Figure 22E. There are

15   gradual changes in growth conditions from the whisker to the layer. Thus there is nucleation on the whiskers without creating defects. There are small nucleation steps and strain effects do not appear to give dislocations. Where the substrate is a III-V material,

20   the important advantage is to create a lattice-mismatched layer on the substrate without getting misfit dislocations.

In a variation, as shown in Figure 22F, gold balls 226 are deposited on the surface from an aerosol, in accordance with the method of Example 1. The epitaxial mask deposit 224 is formed over the balls. Whiskers are 5 then grown, as in Figure 22D.

In a further development in accordance with the invention, it is known that whiskers tend to grow preferentially in the <111>B direction because for gallium arsenide (a zinc blende lattice), the arsenic 10 atom is at the apex of a pyramid with gallium ions at the base of the pyramid, see Figure 23A. A preferred embodiment of the invention is illustrated in Figure 23B, where a substrate 230 of silicon has a serrated surface having V-grooves 232 of microscopic dimensions etched to 15 expose <111> planes. Gold particles 234 are deposited on the surfaces of the V-grooves. GaAs whiskers 236, shown in ghost form in Figure 23C, and grown in accordance with Example 1, will extend perpendicular to the walls of the serrations. These whiskers provide nucleation points for 20 bulk growth of a GaAs layer 238. There are gradual changes in growth conditions from the whisker to the layer. Thus there is nucleation on gallium arsenide without creating defects. Any small nucleation steps and

strain effects do not appear to give dislocations. The

direction of the whiskers, in <111> directions at an

angle to the substrate, forces epitaxial growth in a

certain direction, and takes away the problem of

5   antiphase domains, which has been a problem. Thus this

provides a way of integrating III-V compounds onto

silicon (or other Group IV) substrates, and is cheaper

than existing methods – see for example PCT Published

Patent Application No. WO 02/01648.

10   A further advantage of a V-grooved substrate arises

in connection with the solar cell application of Figure

19, in that the serrated substrate provides multiple

reflections of incident light, and hence an increased

probability of photon capture.

15   Referring now to Figure 24, a preferred embodiment

is described for controlling the orientation of whiskers.

Normally, as described above, whiskers of III-V compounds

grow in the <111>B direction. A problem here is that

such whiskers change more or less randomly between

20   hexagonal (wurtzite) (Figure 24A) and cubic (zinc blende)

(Figure 23A) structures. This gives rise to many

stacking faults. Stacking faults are always a problem

particularly for optical properties, but also for

electrical characteristics. By applying strain to the whisker during formation, by change of growth conditions, the direction of growth of the whisker can be changed to the <100> direction, which gives a cubic lattice

5   structure (zinc blende), which does not have stacking faults.

In Figure 24B, a silicon substrate 240 with a <100> surface has whiskers 242 of, e.g., InP, grown on it. The whiskers start to grow as at 244 in the <111> direction,

10   but shortly after initial growth, operating conditions are changed, by increasing the rate of growth and increasing the temperature and pressure within the CBE apparatus, so that the whisker continues to grow as at 246 in the <100> direction. The point 248 at which

15   direction changes is a <110> facet. The whisker at the transition maintains its epitaxial crystalline nature. The structure of the crystal in segment 246 is hexagonal close packed, which significantly reduces the problem of stacking faults.

20   In an alternative method of growth, a short barrier segment of a wide band gap material, e.g. InAs, is grown at point 248; this has the same effect of changing the subsequent orientation of the whisker.

This embodiment is therefore particularly suitable for the growth of nitrides, e.g. GaN, which preferentially grow as hexagonal lattices, and which are particularly prone to stacking faults. By "forcing" the nitride crystal to grow in cubic form, stacking faults are reduced. Further, where structures are made in accordance with Example 2 with segments of different material along the whisker, micro-cavity structures for gallium nitride lasers can be developed. Nitride systems are quite well suited for whisker growth. The problem with nitrides is that they are filled with dislocations and the lack of suitable substrates. Whiskers can be made with defect-free nitrides, and the problem of lattice matching is not there. A regular FP laser can be made in a nanowhisker less than 300nm length, of the order of 100nm. It is a bottom up structure, which is well suited to reading and writing to DVDs.

Referring now to the embodiment shown in Figure 25, this embodiment relates to field emission tips or Spindt cathodes. These are of use in field emission displays (FED), and many methods have been proposed for making such displays. One prior art arrangement as shown in Figure 25A comprises a silicon substrate 250, with a

surface 252, which is patterned by laser ablation, or the like, to form microscopic or nanometric tips 253. A phosphor screen 254 is positioned adjacent the tips, and a voltage between the tips and the screen generates

5   extremely high field strengths at the tips, which causes current flow into the screen, and thus radiation of visible light from the screen.

In Figure 25B, an embodiment of the invention is shown, comprising an FED, wherein the elements of the

10   display are individually addressable. Etched contact metallisation areas 256 are formed on a silicon substrate 250. Gold seed particles 258 are positioned on each metallisation area, by the method as described in Example 1. The gold particles are used as seeds for

15   whisker growth, in order to grow Si whiskers 259, each whisker extending from a respective metallisation area. A single whisker, as shown, or a group of nanowhiskers, forming a single display element may extend from a respective metallisation area. In addition to being

20   individually addressable, an advantage of this embodiment is that the FED is 100% reliable, in contrast to prior methods, e.g. carbon nanotubes (CNT).

Figure 26 discloses an embodiment for infrared to visible light up-conversion. An image 260 of infrared radiation with a wavelength of 1.55 or 2.5µm is shone on the base surface of a gallium arsenide substrate 262 – a

5 relatively large band gap material which will not interact with the radiation. The other side of the substrate has indium arsenide projecting whiskers 264, grown as described in Example 1, and having a relatively small band gap, which will cause absorption of the

10 photons of the radiation. Whiskers 264 are not however individually addressable, in contrast to Figure 25. A voltage of about 20 - 50 volts is applied between the ends of the whiskers and a nearby fluorescent screen 266, and electrons are generated from the indium arsenide

15 whiskers. Indium arsenide has a bandgap corresponding to 3 microns, and will therefore produce electrons in response to radiation shorter than 3 microns. Gallium phosphide may be used as an alternative, but this has a visible light bandgap. The emitted electrons cause

20 fluorescence to give visible light 268 emitted from the fluorescent screen, and a version of the image, but up-converted to visible light wavelength. The applied

voltage may be raised sufficiently to induce avalanche effects.

Figure 27 discloses an embodiment of the invention in which a whisker 270, 400nm long of GaAs (made in accordance with Example 1) extends from a metallisation contact area 272 on a silicon substrate 274. This dimension is 1/4 of a wavelength of 1.55 micron radiation, and hence the whisker provides a ?/4 resonant antenna for 1.55 micron radiation. Contact area 272 provides a ground plane. The antenna may be positioned to receive radiation 276 in free space; alternatively, it may be positioned adjacent the end of a silica fibre link 278 for detection of radiation in the third optical window.

Referring now to Figure 28, an embodiment of the invention is shown for use in the field of spintronics. Spintronics is a technical field where the properties of electronic devices rely on the transport of electron spin through the device – see for example Scientific American June 2002 pp 52-59, "Spintronics", David D. Awschalom et al. In Figure 28, a whisker 280, formed by the process of Example 1, of a magnetic or semi-magnetic material such as manganese gallium arsenide (semi-magnetic) or

manganese arsenide (ferromagnetic) is formed on a Si

substrate 281. Under an applied voltage V, spin

polarised electrons 283 are emitted from the tip of the

whisker, which makes electrical contact with an

5   electrical contact 284 disposed on a substrate 286. The

spin polarised electrons 283 are used for reading and

writing magnetic storage devices 288 disposed on

substrate 286.

In a further development of this embodiment, a

10   problem is overcome, which is that, with ferromagnetism,

there is normally a lower limit on ferromagnetic domain

width, about 10 - 15nm, below which the ferromagnetism

changes to super-paramagnetism. However when

incorporated in a nanowhisker, in accordance with the

15   method of Example 1, the domain diameter can be reduced,

because of the reduced possibilities for symmetrical

alignment in a 1-dimensional system, which makes it more

difficult for the ions of the material to have more than

one orientation. The material of the whisker can be

20   iron, cobalt, manganese, or an alloy thereof.

Referring now to Figure 29, a further embodiment of

the invention is shown comprising a substrate with an

array of electrodes for implantation into a nerve for

repairing a nerve function, for example the retina of an eye. The electrodes are individually addressable. Etched contact metallisation areas 350 are formed on silicon substrate 352. Gold seed particles 354 are

5   positioned on each metallisation area, by the method as described above. The gold particles are used as seeds for whisker growth, in order to grow silicon whiskers 358, each whisker extending from a respective metallisation area. A single whisker, as shown, or a

10   group of nanowhiskers, forming a single electrode element may extend from a respective metallisation area. In addition to being individually addressable, an advantage of this embodiment is that the electrodes are 100% reliable.

15   Referring now to Figure 30, a further embodiment is shown comprising a nanowhisker 360 formed by the method described above. The whisker is formed of silicon and has a gold particle melt at one end 362. Subsequent to formation of the whisker, the whisker is exposed to an

20   atmosphere at a suitable temperature for oxidation of the silicon. This forms an outer shell 364 of silicon dioxide surrounding the whisker and extending along its length. The gold particle melt 362 remains in an

unoxidised condition. This therefore provides a structure highly suitable for the electrode assembly shown in Figure 29, wherein the electrode has very precise electrical characteristics. The silicon material

5   may be replaced by any other material that can be oxidised.

As an alternative, the whisker 360 may be exposed to an atmosphere of a suitable material for forming a high band gap material as an alternative to the oxidation

10   layer 364.

Referring now to Figure 31, this shows a further embodiment of the invention comprising a silicon base member 370. This base member may be a planar substrate, or just a bar. In any event, a row of nanowhiskers 372

15   is formed from one edge surface of the bar or substrate. The nanowhiskers are regularly spaced apart and project into space. The nanowhiskers may have a coating formed on them for absorbing certain molecular structures. In any event the cantilever beam arrangement may be used for

20   any of the well-known applications for cantilever arrangements for measuring molecular species etc.

Referring to Figure 32 this shows a further embodiment of the invention comprising a molecular

sensing device. A substrate 380, e.g., of silicon

nitride, has an insulating layer 382 formed thereon, with

a conductive surface 384, for example gold. An aperture

386 is formed within the layers 382, 384 and a

5   nanowhisker 388 is formed within the aperture.

This is done essentially by a self-assembly process,

since the aperture is formed in insulating layer 382 and

the gold layer 384 is subsequently deposited. Gold is

therefore in consequence deposited on the base of the

10   aperture, indicated at 389, and upon heating forms a gold

particle melt which enables formation of a nanowhisker

with appropriate conditions. The gold particle melt 389

resides on top of the nanowhisker in the finished

nanowhisker. The nanowhisker height is such that the

15   particle melt 389 is at least approximately co-planar

with the gold surface layer 384.

The natural resilience of the nanowhisker implies

that it has a characteristic frequency of vibration from

side to side in a direction transverse to its length.

20   Oscillation of particle melt 389 can be detected by

voltage or current signals being created in conductive

layer 384. This therefore provides a means of detecting

the frequency of vibration of the nanowhisker 388.

By appropriate activation of the conductive material with an applied voltage, the whisker may be made to mechanically vibrate within the aperture at a certain eigen frequency, for example, in the gigahertz range.

5   This is because, in view of the small dimensions and low currents involved, during the period of a single vibration, a single electron is transferred from one side of the conductive material to the other via the seed particle melt. This creates a current standard

10 generator, where the current I through the conductive material is equal to product of the frequency of vibration f and the charge e of an electron: $I = f \cdot e$. Thus a known reference signal is generated which can be used in appropriate circumstances.

15   In addition, the particle melt 389 may be coated with a receptor substance so as to permit certain molecular species to be absorbed on the surface of the particle melt 389.   This will cause a change in characteristic frequency of the nanowhisker. This change

20 in frequency may be detected and provides a means of computing the weight of the molecular species absorbed on the surface of the melt 389.

Figure 33 shows the tip of a Scanning Tunneling

Microscope (STM) as comprising a nanowhisker 392 of InP

formed on the end of a flexible beam 394 of Silicon.

Beam 394 is formed by etching from a substrate or bar.